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(54) Title: COATING COMPOSITION AND METHOD FOR REDUCING ULTRAVIOLET LIGHT DEGRADATION

(57) Abstract

The present invention relates to a coating composition containing a combination of ultraviolet light absorbing compounds, one or more of which is bound to a polymer, and a method for reducing degradation of coating compositions due to ultraviolet light exposure.

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COATING COMPOSITION AND METHOD FOR REDUCING
ULTRAVIOLET LIGHT DEGRADATION

5

Background of the Invention

The present invention relates to a coating 10 composition containing a combination of polymer-bound ultraviolet light absorbing compounds.

Discussion of the Prior Art

Ultraviolet absorbers are used in coating 15 compositions to reduce the degradation of the coating resulting from the effects of atmospheric oxygen, moisture and ultraviolet light. The degradation is manifest in cracking, loss of gloss, changes in shade, delamination and formation of bubbles in the cured 20 coating films. It is known that stabilizers, such as ultraviolet (uv) absorbers, substantially prevent or minimize such damage in coatings.

Examples of ultraviolet light absorbers include benzotriazoles, 2-hydroxybenzophenones oxanilide, and 25 2-hydroxyphenyltriazines. Benzotriazoles are highly effective ultraviolet light absorbers over a broad spectrum, but these compounds are often not stable and may migrate to other coating layers in a multi-layer coating system or may chemically degrade in the coating 30 composition, thereby losing efficacy as ultraviolet light absorbers. Triazine ultraviolet absorber compounds are more chemically stable, but do not have the range of

ultraviolet light absorption that the benzotriazoles have.

It is an object of the present invention to improve the stability of ultraviolet light absorbers in a coating 5 composition, to enhance ultraviolet light absorption and to reduce degradation of a coating composition due to ultraviolet light exposure.

Summary of the Invention

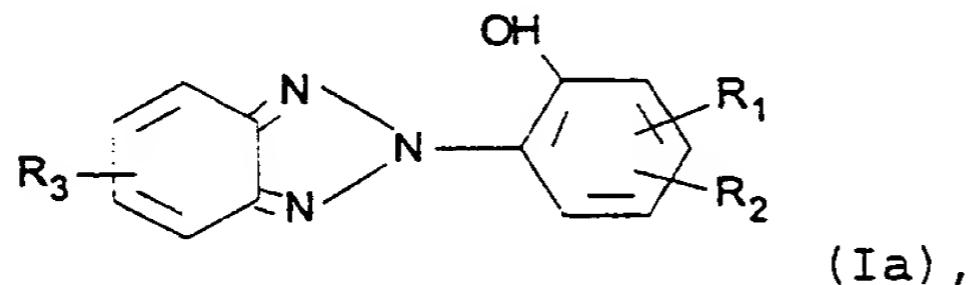
According to the present invention, a polymer-10 bound benzotriazole or polymer-bound triazine is incorporated into a coating composition in combination with at least one other ultraviolet light absorber to improve resistance of a coating composition to ultraviolet light degradation. The polymer-bound 15 benzotriazole or polymer-bound triazine prevents migration of the benzotriazole or triazine from the surface coating and increases its chemical stability in a coating composition, thus providing longer lasting ultraviolet protection. The polymer-bound benzotriazole 20 and polymer-bound triazine may be used in combination with each other, or either one may be used in combination with other ultraviolet absorbers such as non-polymeric benzotriazoles, non-polymeric triazines, 2-hydroxybenzophenone, oxanilide, and mixtures thereof. 25 The benzotriazole and triazine can be added as separate polymers or can be polymerized onto a single polymeric compound. The benzotriazole or triazine can be polymerized onto a polymeric component of the coating composition, whether it is a principal resin, a pigment 30 grind resin, crosslinking agent, rheology modifier, flow additives, or other polymeric components of the coating

composition. In a preferred embodiment the benzotriazole or triazine is polymerized onto the principal crosslinkable resin.

Detailed Description of the Invention

5 Polymer-bound triazine and polymer-bound benzotriazole are incorporated into a coating composition in combination with each other, or used individually with one or more additional ultraviolet light absorbers, to provide longer lasting ultraviolet protection in a
10 coating composition. When a polymer-bound benzotriazole is employed as a UV absorber, it is combined with compounds selected from the group consisting of triazines which may be polymeric or non-polymeric compounds, non-polymeric benzotriazoles, 2-hydroxybenzophenone
15 compounds, oxanilides, and mixtures thereof. Where a polymer bound triazine is used it is combined with polymer-bound or non-polymer bound benzotriazoles, non-polymer bound triazines or other UV absorbers, such as 2-hydroxybenzophenone compounds, oxanilides, and mixtures
20 thereof. The preferred combinations of UV absorber include polymer-bound benzotriazole and triazine which may be polymer-bound or non-polymer bound.

A compound comprising a polymer-bound benzotriazole useful in the present invention is shown in formula (Ia):



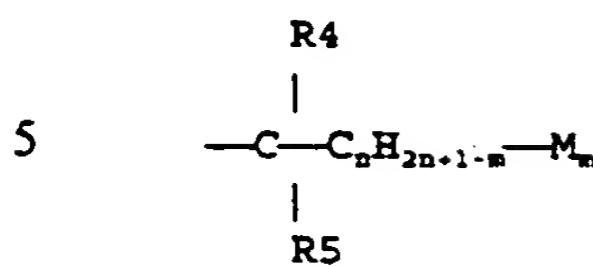
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wherein, in the compounds of the formula (Ia), R₁, R₂ and R₃ can be hydrogen, but at least one of the radicals R₁ and R₂ must be other than hydrogen. Additionally, R₁, R₂

and R_3 can be halogen, hydroxyl halogen methyl, alkyl having 1 to 18 carbons, phenyl alkyl having 1 to 4 carbons in the alkyl moiety, hydroxy alkyl having 1 to 24 carbon atoms in the alkyl chain, such as methyl, ethyl, 5 propyl, butyl, hexyl, octyl, nonyl, dodecyl, tetradecyl, hexadecyl, octadecyl, nonadecyl and eicosyl and also corresponding branched isomers, alkyl substituted by -COOH, -COOY₈, -CONH₂, -CONHY₉, -CONY₉Y₁₀, -NH₂, -NHY₉, -NY₉Y₁₀, -NHCOY₁₁, -CN, and/or -OCOY₁₁, which has 4 to 20 10 carbon atoms, is interrupted by one or more oxygen atoms and is unsubstituted or substituted by hydroxyl or alkoxy having 1 to 12 carbon atoms, alkenyl having 3 to 6 carbon atoms, glycidyl, cyclohexyl which is unsubstituted or substituted by hydroxyl, alkyl having 1 to 4 carbon atoms 15 and/or -OCOY₁₁, phenylalkyl which has 1 to 5 carbon atoms in the alkyl moiety and is unsubstituted or substituted by hydroxyl, chlorine and/or methyl, -COY₁₂ or --SO₂Y₁₃, or, if u is 2, Y₂ is alkylene having 2 to 16 carbon atoms, 20 alkylene having 4 to 12 carbon atoms, xylylene, alkylene which has 3 to 20 carbon atoms, is interrupted by one or more -O- atoms and/or substituted by hydroxyl, -CH₂CH(OH)CH₂-O-Y₁₅, -OCH₂CH(OH)CH₂, -CO-Y₁₆-CO-, 25 -CO-NH-Y₁₇, -NH-CO-, or -(CH₂)_m-CO₂-Y₁₈-OCO-(CH₂)_m, in which m is 1,2 or 3, Y₈ is alkyl having 1 to 18 carbon atoms, amine, alkyl amine or cycloalkyl amine, wherein the alkyl or cycloalkyl has up to 6 carbon atoms, alkenyl having 3 to 18 carbon atoms, alkyl which has 3 to 20 carbon atoms, is interrupted by one or more oxygen or sulfur atoms or -NT₆- and/or is substituted by hydroxyl, alkyl which has 1 30 to 4 carbon atoms and is substituted by -P(O)(OY₁₄)₂, -NY₉Y₁₀ or -OCOY₁₁ and/or hydroxyl, alkenyl having 3 to 18

carbon atoms, glycidyl, or phenylalkyl having 1 to 5 carbon atoms in the alkyl moiety, Y_9 and Y_{10} independently of one another are alkyl having 1 to 12 carbon atoms, alkoxyalkyl having 3 to 12 carbon atoms, 5 dialkylaminoalkyl having 4 to 16 carbon atoms or cyclohexyl having 5 to 12 carbon atoms, or Y_9 and Y_{10} together are alkylene, oxalkylene or azaalkylene having in each case 3 to 9 carbon atoms, Y_{11} is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms or 10 phenyl, Y_{12} is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms, phenyl, alkoxy having 1 to 12 carbon atoms, phenoxy, alkylamino having 1 to 12 carbon atoms or phenylamino, Y_{13} is alkyl having 1 to 18 carbon atoms, phenyl or alkyphenyl having 1 to 8 carbon 15 atoms in the alkyl radical, Y_{14} is alkyl having 1 to 12 carbon atoms or phenyl, Y_{15} is alkylene having 2 to 10 carbon atoms, phenylene or a group -phenylene-M-phenylene- in which M is -O-, -S-, -SO₂-, -CH₂- or -C(CH₃)₂- , Y_{16} is alkylene, oxaalkylene or thiaalkylene having in 20 each case 2 to 10 carbon atoms, phenylene or alkenylene having 2 to 6 carbon atoms, Y_{17} is alkylene having 2 to 10 carbon atoms, phenylene or alkylphenlene having 1 to 11 carbon atoms in the alkyl moiety, and Y_{18} is alkylene having 2 to 10 carbon atoms or alkylene which has 4 to 20 25 carbon atoms and is interrupted once or several times by oxygen.

R_1 may be phenylalkyl having 1 to 4 carbon atoms in the alkyl moiety, for example benzyl, and can also be cycloalkyl having 5 to 8 carbon atoms, for example 30 cyclopentyl, cyclohexyl and cyclooctyl, or a radical of the formula

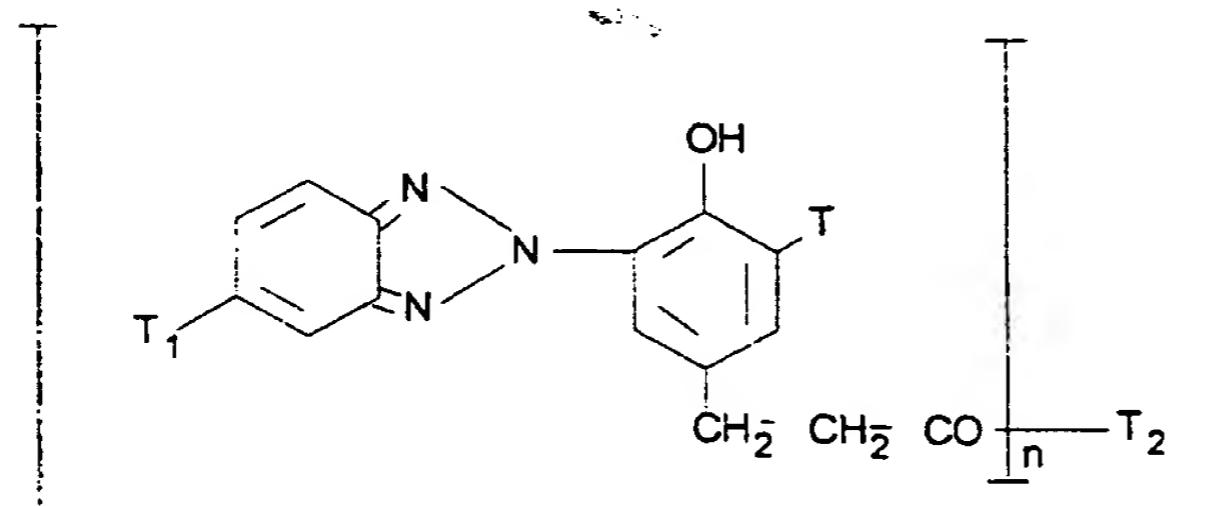


in which R_4 and R_5 independently of one another are alkyl having in each case 1 to 5 carbon atoms, in particular 10 methyl, or R_4 together with the radical $\text{C}_n\text{H}_{2n+1-m}$, forms a cyclolakyl radical having 5 to 12 carbon atoms, for example cyclohexyl, cyclooctyl and cyclodecyl. M is a radical of the formula $-\text{COOR}_6$ in which R_6 is hydrogen, or 15 alkyl having 1 to 12 carbon atoms, or alkoxyalkyl having 1 to 20 carbon atoms in each of the alkyl and the alkoxy moieties. Suitable alkyl radicals R_6 are those enumerated for R_1 . Examples of suitable alkoxyalkyl groups are -
20 $\text{C}_2\text{H}_4\text{OC}_2\text{H}_5$, $-\text{C}_2\text{H}_4\text{OC}_8\text{H}_{17}$ and $-\text{C}_4\text{H}_9\text{OC}_4\text{H}_9$. As phenylalkyl having 1 to 4 carbon atoms, R_6 is, for example, benzyl, cumyl, α -methylbenzyl or phenylbutyl.

At least one of the radicals R_1 and R_2 must be other than hydrogen.

Alternatively, a benzotriazole useful in the present invention has the following formula:

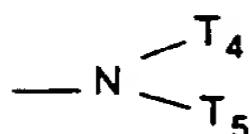
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I (b)

In the compounds of the formula (Ib) T is hydrogen or alkyl having 1 to 6 carbon atoms, such as methyl and

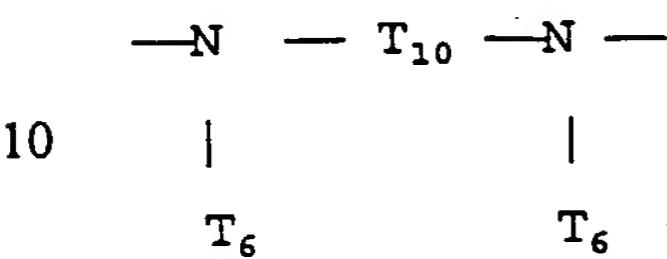
butyl, T_1 is hydrogen, chlorine or alkyl or alkoxy having in each case 1 to 4 carbon atoms, for example methyl, methoxy and butoxy, and n is 1 or 2. If n is 1, T_2 is chlorine or a radical of the formula $-OT_3$, or



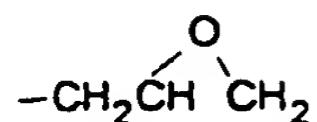
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and if

n is 2, T_2 is a radical of the formula



or $-O-T_3-O-$, where T_3 is hydrogen, alkyl which has 1 to 18 carbon atoms and is unsubstituted or substituted by 1 to 15 3 hydroxyl groups or by $-OCOT_6$, alkyl which has 3 to 18 carbon atoms, is interrupted once or several times by $-O-$ or $-NT_6-$ and is unsubstituted or substituted by hydroxyl or $-OCOT_6$. Examples of T_3 as cycloalkyl include cycloalkyl having 5 to 12 carbon atoms, such as cyclopentyl, cyclohexyl or cyclooctyl and is unsubstituted or substituted by hydroxyl and/or alkyl having 1 to 4 carbon atoms in the alkyl moiety, for example benzyl or phenylbutyl. T_3 can also be alkenyl having 2 to 18 carbon atoms. Suitable alkenyl radicals are derived from the 20 alkyl radicals enumerated in the definitions of R_1 . These alkenyl radicals can be substituted by hydroxyl. Examples of T_3 as phenylalkyl are benzyl, phenylethyl, cumyl, α -methylbenzyl or benzyl. T_3 can also be a radical of the formula $-CH_2C-H(OH)-T$, or

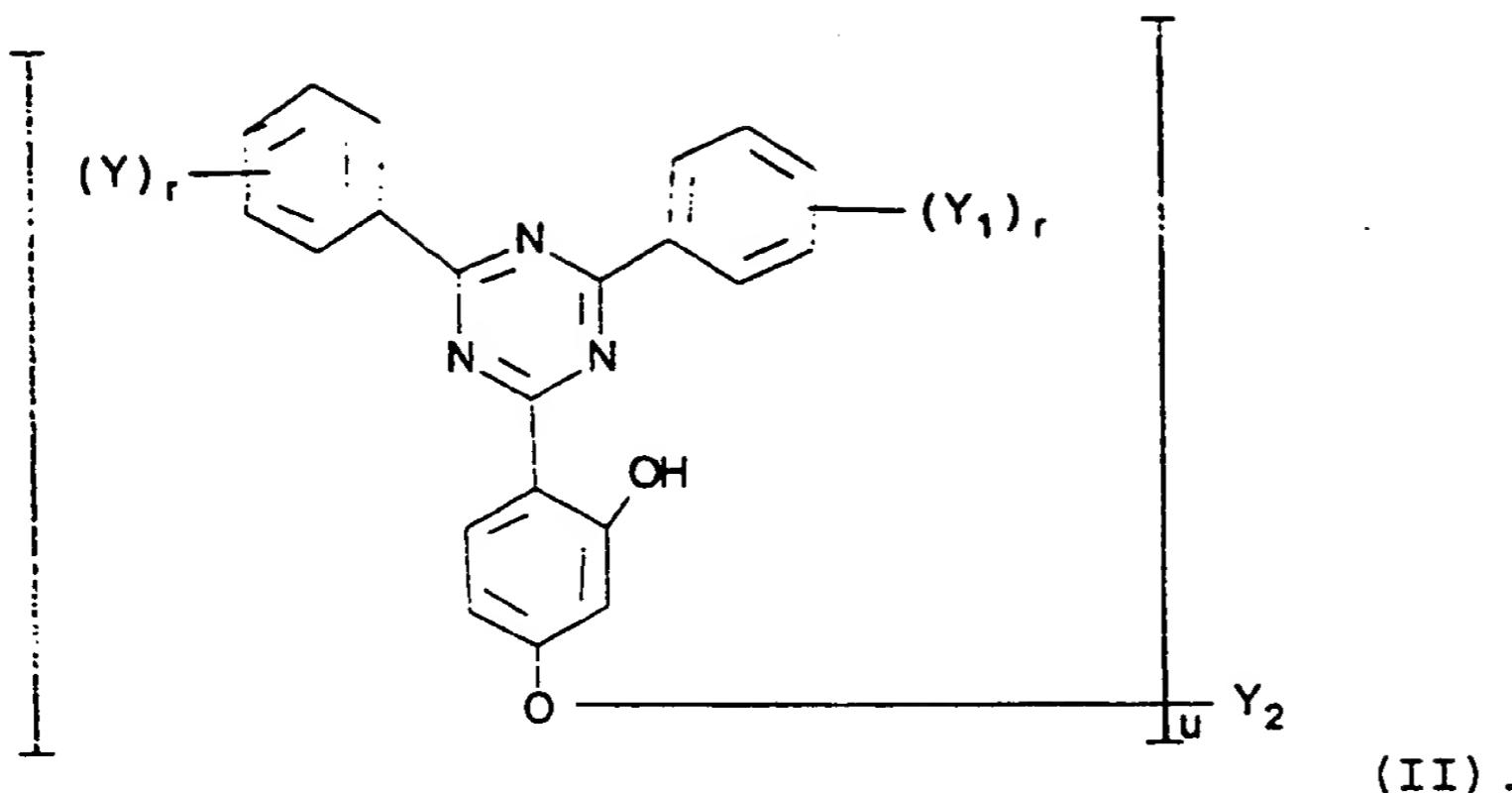


T₄ and T₅ independently of one another are hydrogen, alkyl having 1 to 18 carbon atoms, alkyl which has 3 to 18 carbon atoms and is interrupted once or several times by

5 -O- or

NT₆-, cycloalkyl having 5 to 12 carbon atoms, for example. phenyl, phenyl which is substituted by alkyl having 1 to 4 carbon atoms, alkenyl having 3 to 8 carbon atoms, phenylalkyl having 1 to 4 carbon atoms in the alkyl 10 moiety or hydroxyalkyl having 2 to 4 carbon atoms, T₆ is hydrogen, alkyl having 1 to 18 carbon atoms, cycloalkyl having 5 to 12 carbon atoms, alkenyl having 3 to 8 carbon atoms, phenyl, phenyl which is substituted by alkyl having 1 to 4 carbon atoms, phenylalkyl having 1 to 4 15 carbon atoms in the alkyl moiety, T₇ is hydrogen, alkyl having 1 to 18 carbon atoms, phenyl which is unsubstituted or substituted by hydroxyl, phenylalkyl having 1 to 4 carbon atoms in the alkyl moiety, or -CH₂OT₈, T₈ is alkyl having 1 to 18 carbon atoms, alkenyl 20 having 3 to 8 carbon atoms, cycloalkyl having 5 to 10 carbon atoms, phenyl, phenyl which is substituted by alkyl having 1 to 4 carbon atoms, or phenylalkyl having 1 to 4 carbon atoms in the alkyl.

The 2-hydroxypenyltriazine has the formula



In the compounds of the formula (II), u is 1 to 2 and r is an integer from 1 to 3, the substituted Y_1 independently of one another are hydrogen, hydroxyl 5 halogenomethyl, alkyl having 1 to 12 carbon atoms, alkoxy having 1 to 19 carbon atoms, phenoxy which is unsubstituted or substituted by hydroxyl, alkoxy having 1 to 18 carbon atoms, or halogen, or is substituted by alkyl or alkoxy having in each case 1 to 18 carbon atoms 10 or halogen, alkyl which has 1 to 12 carbon atoms and is substituted by $-COOH$, $-COOY_8$, $-CONH_2$, $-CONHY_9$, $-CONY_9Y_{10}$, $-NH_2$, $-NHY_9$, $-NY_9Y_{10}$, $-NHCOY_{11}$, $-CN$ and/or $-OCOY_{11}$, which has 4 to 20 carbon atoms, is interrupted by one or more oxygen atoms and is unsubstituted or substituted by 15 hydroxyl or alkoxy having 1 to 12 carbon atoms, alkenyl having 3 to 6 carbon atoms, glycidyl, cyclohexyl which is unsubstituted or substituted by hydroxyl, alkyl having 1 to 4 carbon atoms and/or $-OCOY_{11}$, phenylalkyl which has 1 to 5 carbon atoms in the alkyl moiety and is 20 unsubstituted or substituted by hydroxyl, chlorine and/or methyl, $-COY_{12}$ or $-SO_2Y_{13}$, or, if u is 2, Y_2 is alkylene having 2 to 16 carbon atoms, alkylene having 4 to 12 carbon atoms, xylene, alkylene which has 3 to 20 carbon

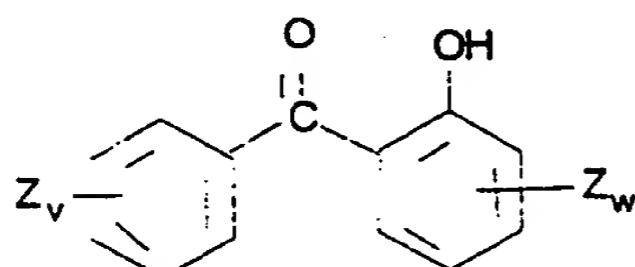
atoms, is interrupted by one or more -O- atoms and/or substituted by hydroxyl,

-CH₂CH(OH)CH₂-O-Y₁₅, -OCH₂CH(OH)CH₂, -CO-Y₁₆-CO-,
-CO-NH-Y₁₇-NH-CO-, or -(CH₂)_m-CO₂-Y₁₈-OCO-(CH₂)_m, in which m
5 is 1,2 or 3, Y₈ is alkyl having 1 to 18 carbon atoms, amine, alkyl amine or cycloalkyl amine wherein the alkyl or cycloalkyl group has up to six carbon atoms, alkenyl having 3 to 18 carbon atoms, alkyl which has 3 to 20 carbon atoms, is interrupted by one or more oxygen or
10 sulfur atoms or -NT₆- and/or is substituted by hydroxyl, alkyl which has 1 to 4 carbon atoms and is substituted by -P(O)(OY₁₄)₂,

-NY₉Y₁₀ or -OCOY₁₁ and/or hydroxyl, alkenyl having 3 to 18 carbon atoms, glycidyl, or phenylalkyl having 1 to 5
15 carbon atoms in the alkyl moiety, Y₉ and Y₁₀ independently of one another are alkyl having 1 to 12 carbon atoms, alkoxyalkyl having 3 to 12 carbon atoms, dialkylaminoalkyl having 4 to 16 carbon atoms or cyclohexyl having 5 to 12 carbon atoms, or Y₉ and Y₁₀
20 together are alkylene, oxalkylene or azaalkylene having in each case 3 to 9 carbon atoms, Y₁₁ is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms or phenyl, Y₁₂ is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms, phenyl, alkoxy having 1 to
25 12 carbon atoms, phenoxy, alkylamino having 1 to 12 carbon atoms or phenylamino, Y₁₃ is alkyl having 1 to 18 carbon atoms, phenyl or alkyphenyl having 1 to 8 carbon atoms in the alkyl radical, Y₁₄ is alkyl having 1 to 12 carbon atoms or phenyl, Y₁₅ is alkylene having 2 to 10
30 carbon atoms, phenylene or a group -phenylene-M-phenylene- in which M is -O-, -S-, -SO₂-, -CH₂- or -C(CH₃)₂-

, Y_{16} is alkylene, oxaalkylene or thiaalkylene having in each case 2 to 10 carbon atoms, phenylene or alkenylene having 2 to 6 carbon atoms, Y_{17} is alkylene having 2 to 10 carbon atoms, phenylene or alkylphenylene having 1 to 11 carbon atoms in the alkyl moiety, and Y_{18} is alkylene having 2 to 10 carbon atoms or alkylene which has 4 to 20 carbon atoms and is interrupted once or several times by oxygen.

The 2-hydroxybenzophenone has the formula



10

In the formula v is an integer from 1 to 3 and w is 1 or 2 and the substituents Z independently of one another are hydrogen, alkyl, alkoxy or alkylthio having in each case 1 to 22 carbon atoms, phenoxy or phenylthio.

15

The polymer-bound ultraviolet light absorber compounds are reacted onto polymers by addition polymerization, condensation or rearrangement reactions, or grafting. The UVA compounds may be reacted onto the same polymer or separate polymers. Examples of polymers in which it can be incorporated are:

20

polyolefins, polyacrylates, polymethacrylates, polystyrene, derivatized polystyrenes, polyurethanes, epoxy, polyester, polyether, alkyd and carbamate polymers, and mixtures thereof.

25

The polymer-bound benzotriazole is effective for absorbing UV light in the range of about 200 nm to about 450 nm, particularly in the range of 240 nm to 420 nm. In the preferred embodiment, the benzotriazole is

polymerized onto the principal resin or crosslinker used in the coating composition. Alternatively, the benzotriazole is polymerized onto a pigment grind resin, or other compound used in the coating composition.

5 The polymer-bound ultraviolet light absorber is incorporated into the coating composition in an amount between 0.1 and 30.0 percent by weight, preferably between 1.0 and 10.0 percent by weight, based on total coating composition weight.

10 The invention is illustrated by the following non-limiting examples.

Examples

Example 1

15 Acrylic Polymer-Bound Benzotriazole

Polymer-bound Ultraviolet Light Absorber

A polymer-bound ultraviolet light absorber containing 2.0% benzotriazole, based on total coating solids, was prepared by polymerizing 28.4 grams of a 20 benzotriazole, sold under the trademark Norbloc™ 7966, available from Noramco, Inc. onto 1514.3 grams of a hydroxy functional carbamate resin, sold under the trademark Ureclear®, commercially available from BASF Corporation. The hydroxy functional carbamate resin had 25 a hydroxy equivalency of 1650 g/equivalent at 95% non-volatile content.

Example 2**Coating Composition Containing Polymer-Bound Benzotiazole**

Ingredient	Amount*
Acrylic resin from Ex. 1	75.51
² Resimine 747 Aminoplast	20.66
Acid Catalyst	1.00
Fumed Silica Rheology Control Additive	1.31
Flow Control Additive	0.20
Adhesion promoter	1.32
Total	100.00

5 *All weights are in percent by weight based on total solid content of coating.

Example 3**Coating Composition Containing Polymer-bound
10 Benzotriazole and Triazine Mixture**

To the coating composition in Example 2 were added 2.1 grams of 2-hydroxyphenyl triazine. The triazine was used in a 72% solution of triazine and solvent. The 15 resultant coating composition comprised 1% by weight based on coating composition solids content.

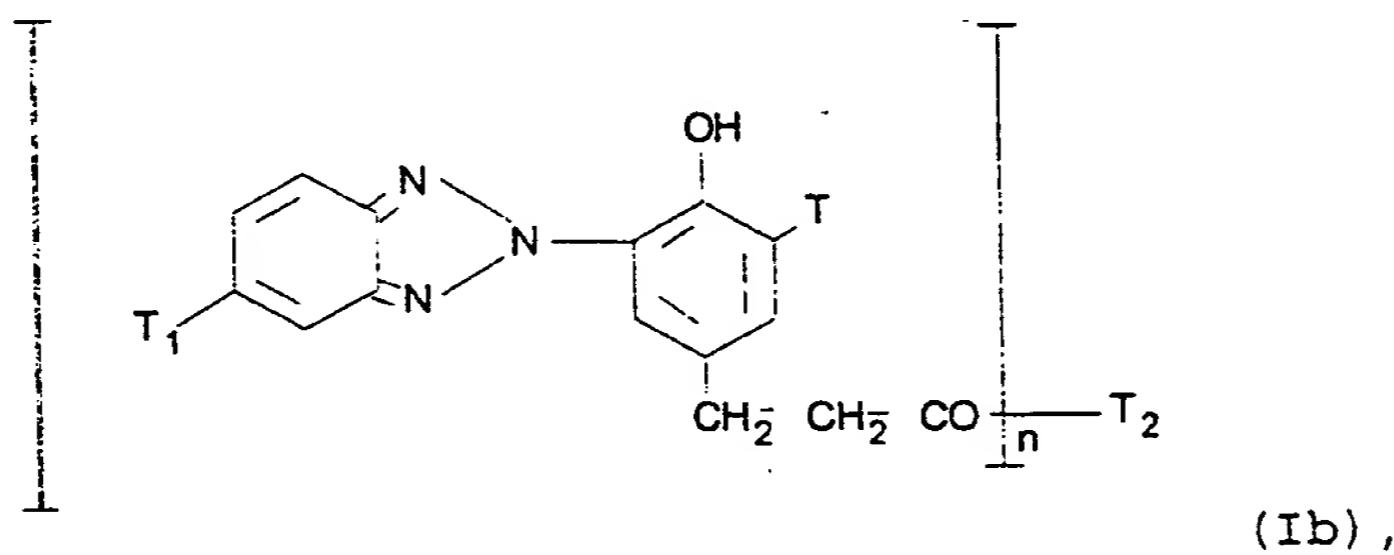
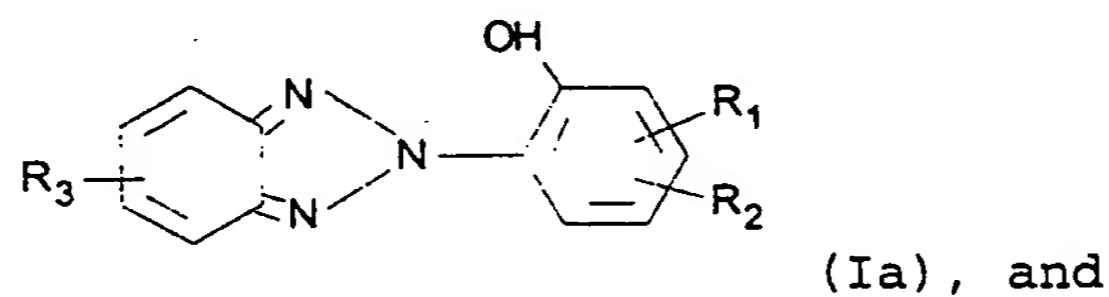
Example 4**Coating Composition Containing Polymer-bound
20 Benzotriazole, Triazine and Hindered Amine Light Stabilizer (HALS)**

To the coating composition in Example 2 was added 2-hydroxyphenyl triazine in an amount of 2.1 grams and a 25 hindered amine light stabilizer (HALS) sold under the trademark Sandivar 3058 and available from Sandoz, in an amount of 1.5% based on total solids content of the coating composition. The HALS is used in a 95% solution, where the solution comprises HALS and solvent.

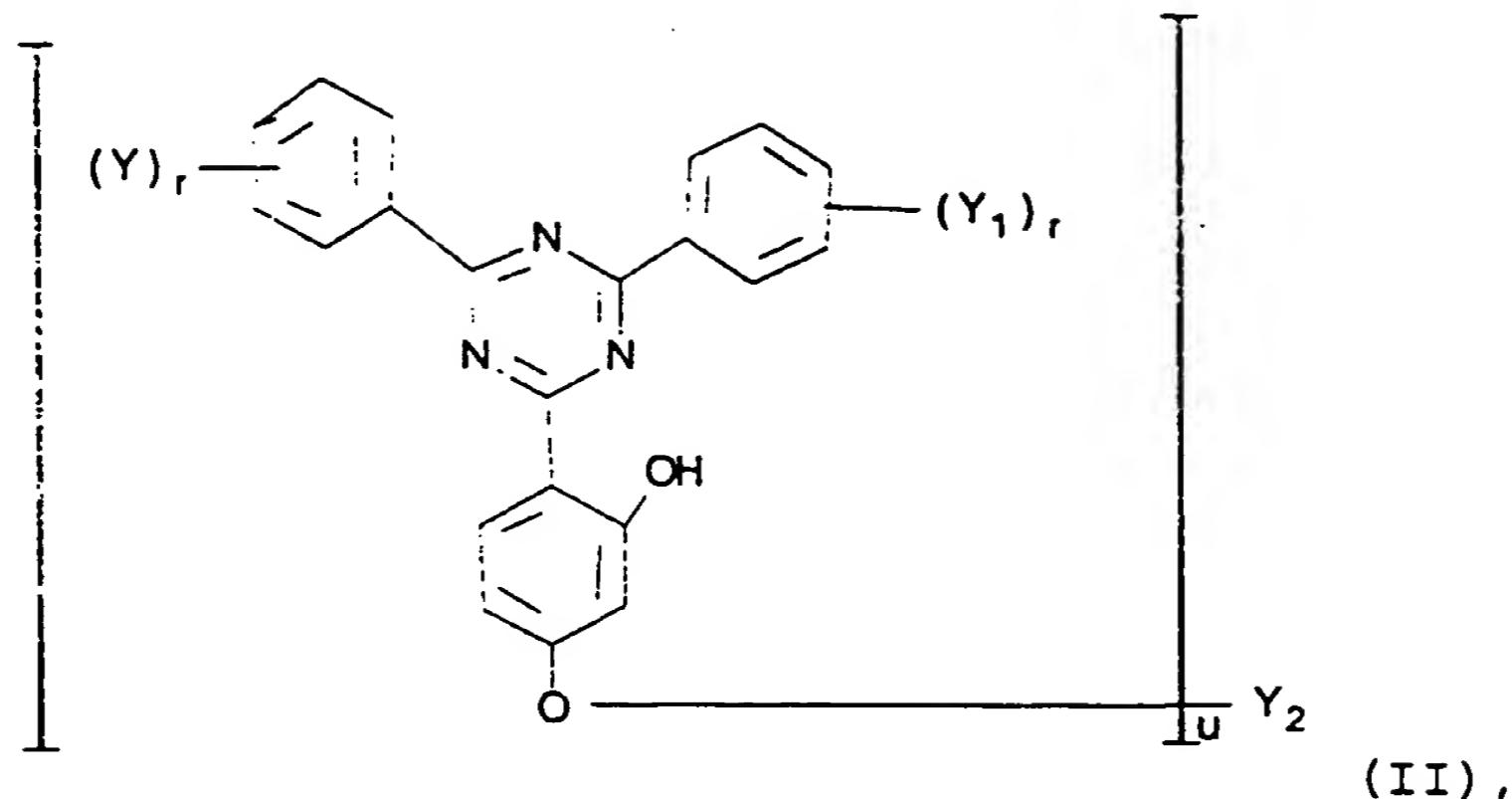
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I Claim:

1. A coating composition comprising
 - a) a crosslinkable principal resin and
 - 5 b) a combination of ultraviolet light absorbing compounds, wherein at least one ultraviolet light absorber is a polymer-bound ultraviolet light absorber selected from the group consisting of polymer-bound
- 10 benzotriazoles having the formula



- 15 polymer-bound 2-hydroxyphenyl triazines having the formula (II)



and mixtures thereof,

used in combination with a non-polymer bound ultraviolet light absorber selected from the group consisting of non-polymeric 2-hydroxy phenyl triazines, non-polymeric benzotriazoles, 2-hydroxybenzophenones, oxanilide, and mixtures thereof,

wherein in the compounds of the formula (Ia),
 10 R_1 is selected from the group consisting of hydrogen, alkyl having 1 to 24 carbon atoms, phenylalkyl having 1 to 4 carbon atoms in the alkyl moiety, and R_2 is selected from the group consisting of hydrogen, halogen, alkyl having 1 to 18 carbons, phenyl alkyl having 1 to 4 carbons in the alkyl moiety,
 15 R_3 is selected from the group consisting of hydrogen, chlorine, alkyl having 1 to 4 carbon atoms; with at least one of the radicals R_1 and R_2 being other than hydrogen; in formula (Ib) T is hydrogen or alkyl having 1 to 6 carbon atoms,
 20 T_1 is hydrogen, chlorine or alkyl having 1 to 4 carbon atoms, and n is 1 or 2,
 when n is 1, T_2 is chlorine or a radical of the formula

-OT₃, where T₃ is hydrogen, alkyl which has 1 to 18 carbon atoms and is unsubstituted or substituted by 1 to 3 hydroxyl groups; alkyl which has 3 to 18 carbon atoms interrupted once or several times by -O- and is 5 unsubstituted or substituted by hydroxyl; alkenyl which has 2 to 18 carbon atoms and is unsubstituted or substituted by hydroxyl; phenylalkyl having 1 to 4 carbon atoms in the alkyl moiety, or a radical of the formula -CH₂CH(OH)-T₁, or glycidyl;

10 where T₁ is hydrogen, alkyl having 1 to 18 carbon atoms, phenyl which is unsubstituted or substituted by hydroxyl; and if n is 2, T₂ is a radical of the formula -O-T₃-O-, T₃ is alkylene having 2 to 8 carbon atoms, alkenylene having 4 to 8 carbon atoms, cyclohexylene, alkylene which 15 has 2 to 18 carbon atoms and is interrupted once or several times by -O-,

in the formula (IIa)

u is 1 to 2,

r is an integer from 1 to 3,

20 the substituents Y₁ independently of one another are hydrogen, hydroxyl, halogen, halogenomethyl, alkyl having 1 to 12 carbon atoms, alkoxy having 1 to 18 carbon atoms, when u is 1, Y₂ is alkyl having 1 to 18 carbon atoms, alkyl which has 1 to 12 carbon atoms and is substituted 25 by -COOH

-COOY₈, -CONH₂, CONHY₉, -ONY₉Y₁₀, -CN, -OCOY₁₁, or mixtures thereof; alkyl which has 4 to 20 carbon atoms which is interrupted by one or more oxygen atoms and is unsubstituted or substituted by hydroxyl or alkoxy having 30 1 to 12 carbon atoms; alkenyl having 3 to 6 carbon atoms, glycidyl, phenylalkyl which has 1 to 5 carbon atoms in

the alkyl moiety and is unsubstituted or substituted by hydroxyl, chlorine and or methyl; -COY₁₂ or SO₂ Y₁₃, wherein Y₈ is alkyl having 1 to 18 carbon atoms, amine, alkylamine or cycloalkylamine wherein the alkyl or 5 cycloalkyl group has up to 6 carbon atoms, alkenyl having 3 to 18 carbon atoms, alkyl which has 3 to 20 carbon atoms, and is interrupted by one or more oxygen atoms, or said alkyl substituted by substituted by hydroxyl; alkenyl having 3 to 18 carbon atoms, glycidyl or 10 phenylalkyl having 1 to 5 carbon atoms in the alkyl moiety,

Y₉ and Y₁₀ independently of one another are alkyl having 1 to 12 carbon atoms, alkoxyalkyl having 3 to 12 carbon atoms, dialkylaminoalkyl having 4 to 16 carbon atoms or 15 cyclohexyl having 5 to 12 carbon atoms,

Y₁₁ is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms or phenyl,

Y₁₂ is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms, phenyl, alkoxy having 1 to 12 carbon 20 atoms, phenoxy, alkylamino having 1 to 12 carbon atoms or phenylamino,

Y₁₃ is alkyl having 1 to 18 carbon atoms, phenyl or alkylphenyl having 1 to 8 carbon atoms in the alkyl radical; and when u is 2, Y₂ is alkylene having 2 to 16 25 carbon atoms, alkylene having 4 to 12 carbon atoms and is interrupted by one or more -O- atoms and/or is substituted by hydroxyl; -CH₂CH(OH)CH₂-O-Y₁₅ -OCH₂CH(OH)CH₂, or

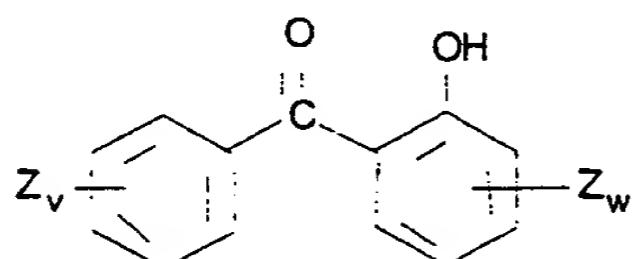
-(CH₂)_m-CO₂-Y₁₆-OCO-(CH₂)_m, in which m is 1,2 or 3,

Y_{15} is alkylene having 2 to 10 carbon atoms, phenylene or a group -phenylene-M-phenylene- in which M is -O-, -S-, - SO_2 -, - CH_2 - or - $C(CH_3)_2$ -, and Y_{18} is alkylene having 2 to 10 carbon atoms or 5 alkylene which has 4 to 20 carbon atoms and is interrupted once or several times by oxygen.

2. The coating composition of claim 1 wherein the combination of ultraviolet absorbing compounds comprise a 10 polymeric benzotriazole in combination with polymer-bound 2-hydroxyphenyl triazines.

3. The coating composition of claim 2 wherein the combination of ultraviolet absorbing compounds further 15 comprise compounds selected from the group consisting of non-polymeric 2-hydroxyphenyl triazine, non-polymeric benzotriazoles, non-polymeric oxanilide, non-polymeric of 2-hydroxybenzophenones and mixtures thereof.

20 4. The coating composition of claim 1 wherein the combination of ultraviolet light absorbing compounds further comprises a polymeric light absorbing compound having the formula:



25 where v is an integer from 1 to 3 and w is 1 or 2 and the substituents Z independently of one another are hydrogen, halogen, hydroxy or alkoxy having 1 to 12 carbon atoms.

5. The coating composition of claim 1 wherein the ultraviolet absorbing compounds are polymerized onto components of the coating composition, selected from the group consisting of a principal resin, a crosslinker, and
5 mixtures thereof.

6. The coating composition of claim 1 wherein the polymeric principal resin is selected from the group consisting of acrylate, methacrylate, urethane,
10 carbamate, polyester, polyether, polystyrene, derivatized polystyrene, polyolefins, alkyd, and epoxy polymeric resins, and mixtures thereof.

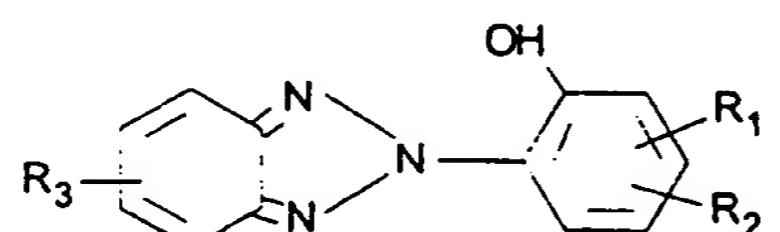
7. The coating composition of claim 1 further
15 comprising a crosslinker selected from the group consisting of isocyanates, ureas, aminoplasts, carbamates and mixtures thereof.

8. The coating composition of claim 1 or 2, wherein the
20 2-hydroxyphenylbenzotriazole or triazine is copolymerized with a principal acrylate resin having hydroxy functionality and the coating composition includes an aminoplast crosslinker.

25 9. The coating composition of claim 1 wherein the coating is a clearcoat coating composition.

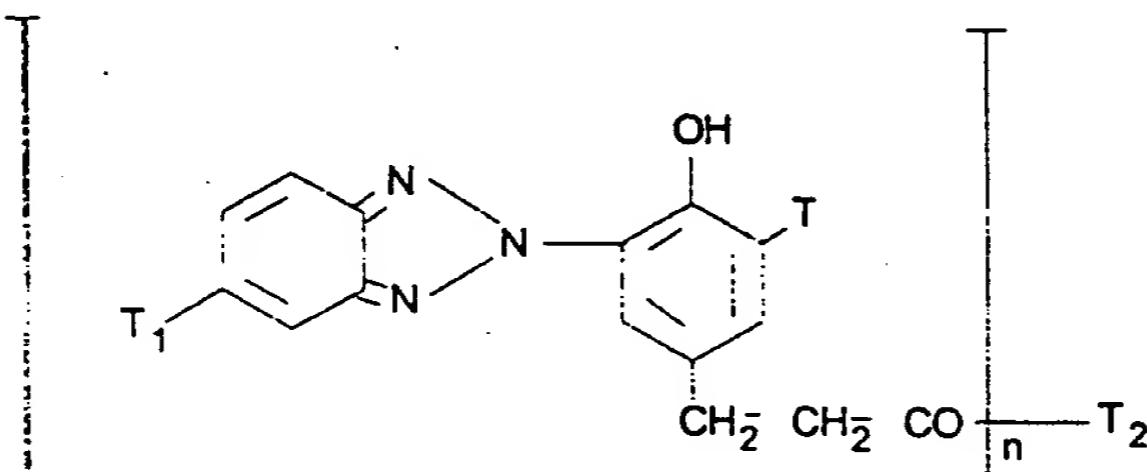
10. A method for improving the ultraviolet radiation absorption of a coating composition, comprising the step
30 of adding to a coating composition a combination of ultraviolet light absorbing compounds, wherein at least

one ultraviolet light absorber is a polymer-bound ultraviolet light absorber selected from the group consisting of polymer-bound benzotriazoles having the formula



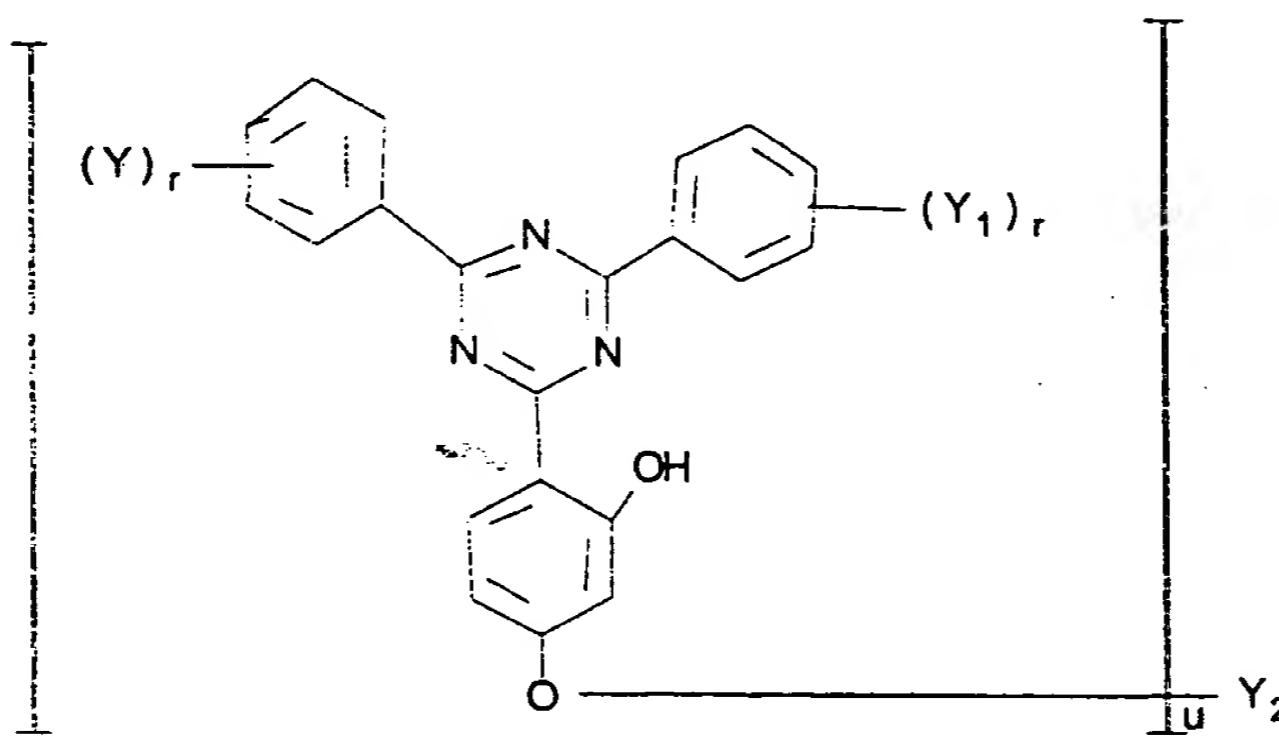
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(Ia), and



(Ib),

polymer-bound 2-hydroxyphenyl triazines having the formula (IIa)



(IIa),

10

and mixtures thereof,

used in combination with a non-polymer bound ultraviolet light absorber selected from the group consisting of benzotriazoles, 2-hydroxy phenyl triazines, 2-hydroxybenzophenones, oxanilide, and mixtures thereof,

15

wherein in the compounds of the formula (Ia),
R₁ is hydrogen, alkyl having 1 to 24 carbon atoms,
phenylalkyl having 1 to 4 carbon atoms in the alkyl
moiety,

5 R₂ is H, halogen, or alkyl having 1 to 18 carbon atoms,
phenyl alkyl having 1 to 4 carbon atoms in the alkyl
moiety

R₃ is H, chlorine, alkyl or alkoxy, having in each case 1
to 4 carbon atoms,

10 in formula (Ib) T is hydrogen or alkyl having 1 to 6
carbon atoms,

T₁ is hydrogen, chlorine or alkyl having 1 to 4 carbon
atoms, and n is 1 or 2,
when n is 1, T₂ is chlorine or a radical of the formula
15 -OT₃, where T₃ is hydrogen, alkyl which has 1 to 18 carbon
atoms and is unsubstituted or substituted by 1 to 3
hydroxyl groups; alkyl which has 3 to 18 carbon atoms
interrupted once or several times by -O- and is
unsubstituted or substituted by hydroxyl; alkenyl which
20 has 2 to 18 carbon atoms and is unsubstituted or
substituted by hydroxyl; phenylalkyl having 1 to 4 carbon
atoms in the alkyl moiety, or a radical of the formula -
CH₂CH(OH)-T₇ or glycidyl;

where T₇ is hydrogen, alkyl having 1 to 18 carbon atoms,
25 phenyl which is unsubstituted or substituted by hydroxyl;
and if n is 2, T₂ is a radical of the formula -O-T₉-O-,
T₉ is alkylene having 2 to 8 carbon atoms, alkenylene
having 4 to 8 carbon atoms, cyclohexylene, alkylene which
has 2 to 18 carbon atoms and is interrupted once or
30 several times by -O-,
in the formula (IIa)

u is 1 to 2,

r is an integer from 1 to 3,

the substituents Y_1 independently of one another are hydrogen, hydroxyl, halogen, halogenomethyl, alkyl having

5 1 to 12 carbon atoms, alkoxy having 1 to 18 carbon atoms, when u is 1, Y_2 is alkyl having 1 to 18 carbon atoms, alkyl which has 1 to 12 carbon atoms and is substituted by -COOH

-COO Y_8 , -CONH₂, CONHY₉, -ONY₉Y₁₀, -CN, -OCOY₁₁, or mixtures

10 thereof; alkyl which has 4 to 20 carbon atoms which is interrupted by one or more oxygen atoms and is unsubstituted or substituted by hydroxyl or alkoxy having 1 to 12 carbon atoms; alkenyl having 3 to 6 carbon atoms, glycidyl, phenylalkyl which has 1 to 5 carbon atoms in 15 the alkyl moiety and is unsubstituted or substituted by hydroxyl, chlorine and or methyl; -COY₁₂ or SO₂Y₁₃,

wherein Y_8 is alkyl having 1 to 18 carbon atoms, amine, alklyamine or cycloalkylamine wherein the alkyl or cycloalkyl portion has up to 6 carbon atoms, alkenyl

20 having 3 to 18 carbon atoms, alkyl which has 3 to 20 carbon atoms, and is interrupted by one or more oxygen atoms, or said alkyl substituted by substituted by hydroxyl; alkenyl having 3 to 18 carbon atoms, glycidyl or phenylalkyl having 1 to 5 carbon atoms in the alkyl 25 moiety,

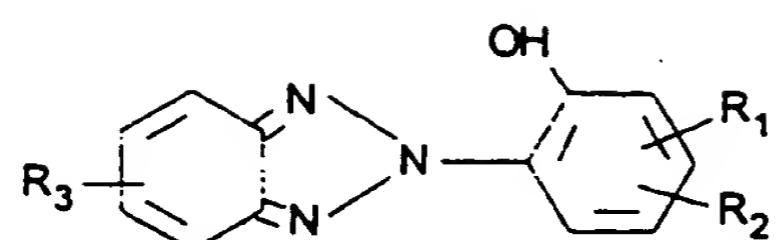
Y_9 and Y_{10} independently of one another are alkyl having 1 to 12 carbon atoms, alkoxyalkyl having 3 to 12 carbon atoms, dialkylaminoalkyl having 4 to 16 carbon atoms or cyclohexyl having 5 to 12 carbon atoms,

30 Y_{11} is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms or phenyl,

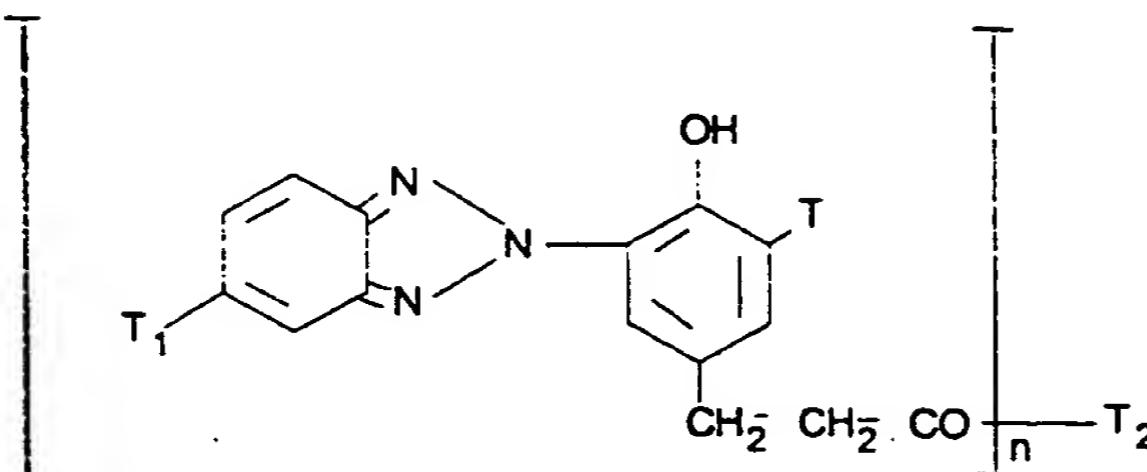
Y_{12} is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms, phenyl, alkoxy having 1 to 12 carbon atoms, phenoxy, alkylamino having 1 to 12 carbon atoms or phenylamino,

5 Y_{13} is alkyl having 1 to 18 carbon atoms, phenyl or alkylphenyl having 1 to 8 carbon atoms in the alkyl radical; and when u is 2, Y_2 is alkylene having 2 to 16 carbon atoms, alkylene having 4 to 12 carbon atoms and is interrupted by one or more -O- atoms and/or is
10 substituted by hydroxyl; $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-\text{O}-Y_{15}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2$, or $-(\text{CH}_2)_m-\text{CO}_2-Y_{18}-\text{OCO}-(\text{CH}_2)_m$, in which m is 1,2 or 3,
 Y_{15} is alkylene having 2 to 10 carbon atoms, phenylene or a group -phenylene-M-phenylene- in which M is -O-, -S-, - SO_2- , - CH_2- or $-\text{C}(\text{CH}_3)_2-$,
15 and Y_{18} is alkylene having 2 to 10 carbon atoms or alkylene which has 4 to 20 carbon atoms and is interrupted once or several times by oxygen.

11. A method for improving the ultraviolet radiation
20 absorption of the clearcoat of a color plus clear composite coating comprising the step of adding to the clearcoat, a combination of ultraviolet light absorbing compounds, wherein at least one ultraviolet light absorber is a polymer-bound ultraviolet light absorber
25 selected from the group consisting of polymer-bound benzotriazoles having the formula

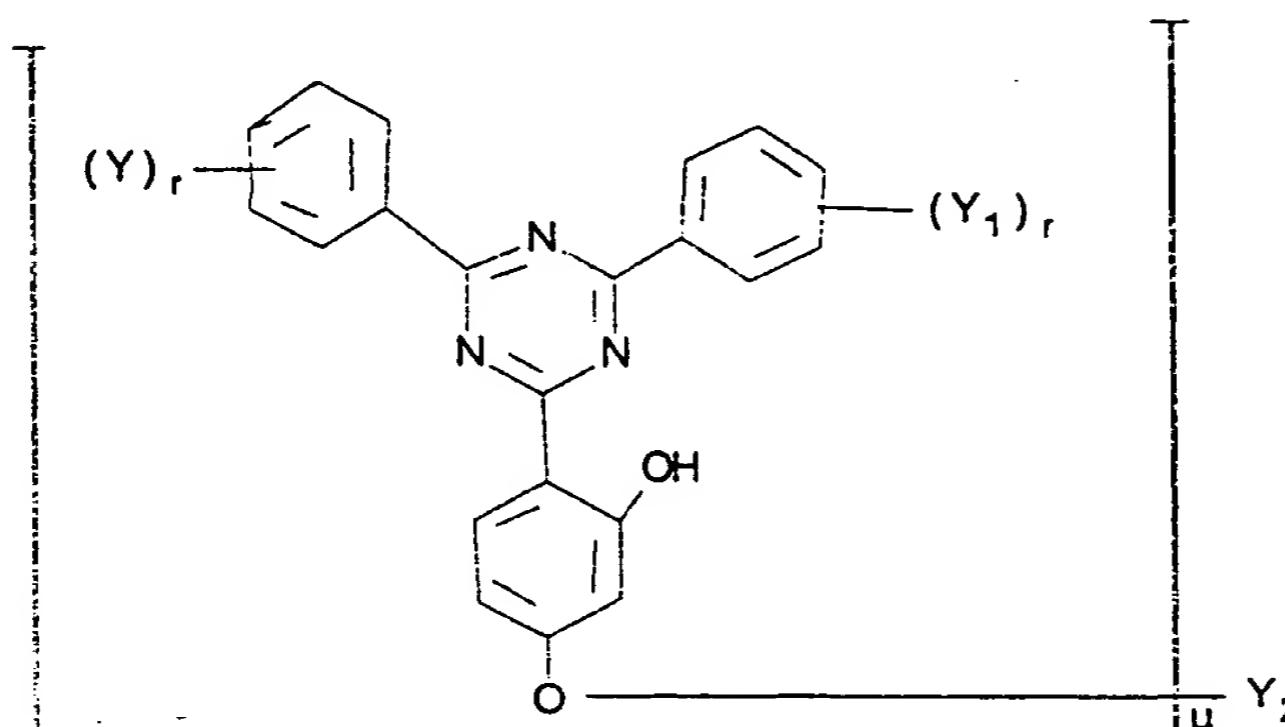


(Ia), and



(Ib),

polymer-bound 2-hydroxyphenyl triazines having the formula (IIa)



(II),

5

and mixtures thereof,

used in combination with a non-polymer bound ultraviolet light absorber selected from the group consisting of benzotriazoles, 2-hydroxy phenyl triazines, 2-hydroxybenzophenones, oxanilide, and mixtures thereof,

10

where in formula (Ia)

R₁ is hydrogen, alkyl having 1 to 24 carbon atoms, phenylalkyl having 1 to 4 carbon atoms in the alkyl

15 moiety,

R₂ is H, halogen, or alkyl having 1 to 18 carbon atoms, phenyl alkyl having 1 to 4 carbon atoms in the alkyl moiety

R₃ is H, chlorine, alkyl or alkoxy, having in each case 1 to 4 carbon atoms,

in formula (Ib) T is hydrogen or alkyl having 1 to 6 carbon atoms,

T₁ is hydrogen, chlorine or alkyl having 1 to 4 carbon atoms, and n is 1 or 2,

when n is 1, T₂ is chlorine or a radical of the formula -OT₃, where T₃ is hydrogen, alkyl which has 1 to 18 carbon atoms and is unsubstituted or substituted by 1 to 3 hydroxyl groups; alkyl which has 3 to 18 carbon atoms

interrupted once or several times by -O- and is unsubstituted or substituted by hydroxyl; alkenyl which has 2 to 18 carbon atoms and is unsubstituted or substituted by hydroxyl; phenylalkyl having 1 to 4 carbon atoms in the alkyl moiety, or a radical of the formula -CH₂CH(OH)-T₇ or glycidyl;

where T₇ is hydrogen, alkyl having 1 to 18 carbon atoms, phenyl which is unsubstituted or substituted by hydroxyl; and if n is 2, T₂ is a radical of the formula -O-T₉-O-, T₉ is alkylene having 2 to 8 carbon atoms, alkenylene having 4 to 8 carbon atoms, cyclohexylene, alkylene which has 2 to 18 carbon atoms and is interrupted once or several times by -O-;

in formula IIIa

u is 1 to 2,

30 r is an integer from 1 to 3,

the substituents Y_1 independently of one another are hydrogen, hydroxyl, halogen, halogenomethyl, alkyl having 1 to 12 carbon atoms, alkoxy having 1 to 18 carbon atoms, when u is 1, Y_2 is alkyl having 1 to 18 carbon atoms, 5 alkyl which has 1 to 12 carbon atoms and is substituted by -COOH

-COO Y_8 , -CONH₂, CONHY₉, -ONY_{9, Y_{10} , -CN, -OCOY₁₁, or mixtures thereof; alkyl which has 4 to 20 carbon atoms which is interrupted by one or more oxygen atoms and is 10 unsubstituted or substituted by hydroxyl or alkoxy having 1 to 12 carbon atoms; alkenyl having 3 to 6 carbon atoms, glycidyl, phenylalkyl which has 1 to 5 carbon atoms in the alkyl moiety and is unsubstituted or substituted by hydroxyl, chlorine and or methyl; -COY₁₂ or SO₂Y₁₃,}

15 wherein Y_8 is alkyl having 1 to 18 carbon atoms, amine, alkylamine or cycloalkylamine wherein the alkyl or cycloalkyl group contains up to 6 carbon atoms, alkenyl having 3 to 18 carbon atoms, alkyl which has 3 to 20 carbon atoms, and is interrupted by one or more oxygen 20 atoms, or said alkyl substituted by substituted by hydroxyl; alkenyl having 3 to 18 carbon atoms, glycidyl or phenylalkyl having 1 to 5 carbon atoms in the alkyl moiety,

Y_9 and Y_{10} independently of one another are alkyl having 1 25 to 12 carbon atoms, alkoxyalkyl having 3 to 12 carbon atoms, diallylaminoalkyl having 4 to 16 carbon atoms or cyclohexyl having 5 to 12 carbon atoms,

Y_{11} is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms or phenyl,

30 Y_{12} is alkyl having 1 to 18 carbon atoms, alkenyl having 2 to 18 carbon atoms, phenyl, alkoxy having 1 to 12 carbon

atoms, phenoxy, alkylamino having 1 to 12 carbon atoms or phenylamino,

Y_{13} is alkyl having 1 to 18 carbon atoms, phenyl or alkylphenyl having 1 to 8 carbon atoms in the alkyl

5 radical; and when u is 2, Y_2 is alkylene having 2 to 16 carbon atoms, alkylene having 4 to 12 carbon atoms and is interrupted by one or more -O- atoms and/or is substituted by hydroxyl; $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-\text{O}-Y_{15}-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2$,

or $-(\text{CH}_2)_m-\text{CO}_2-Y_{18}-\text{OCO}-(\text{CH}_2)_m$, in which m is 1,2 or 3,

10 Y_{15} is alkylene having 2 to 10 carbon atoms, phenylene or a group -phenylene-M-phenylene- in which M is -O-, -S-, -

SO_2- , $-\text{CH}_2-$ or $-\text{C}(\text{CH}_3)_2-$,

and Y_{18} is alkylene having 2 to 10 carbon atoms or alkylene which has 4 to 20 carbon atoms and is

15 interrupted once or several times by oxygen.

12. The method of claim 10 or 11 wherein the combination of ultraviolet absorbing compounds comprise a polymeric benzotriazole in combination with polymer-bound 2-

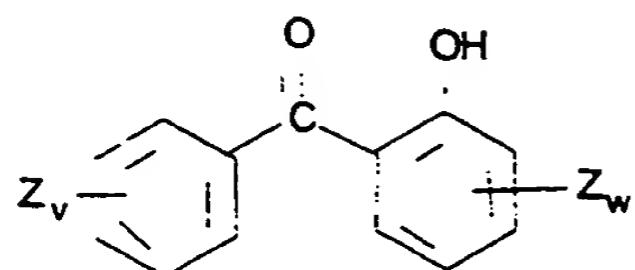
20 hydroxyphenyl triazines.

13. The method of claim 12 wherein the combination of ultraviolet absorbing compounds further comprise compounds selected from the group consisting of non-

25 polymeric 2-hydroxyphenyl triazine, non-polymeric benzotriazoles, non-polymeric oxanilide, non-polymeric of 2-hydroxybenzophenones and mixtures thereof.

14. The method of claim 10 or 11 wherein the combination 30 of ultraviolet light absorbing compounds further

comprises a polymeric light absorbing compound having the formula:



where v is an integer from 1 to 3 and w is 1 or 2 and the
5 substituents Z independently of one another are hydrogen,
halogen, hydroxy or alkoxy having 1 to 12 carbon atoms.

15. The method of claim 10 or 11, wherein the
ultraviolet absorbing compounds are polymerized onto a
10 component of the coating composition, selected from the
group consisting of a principal resin, crosslinker, and
mixtures thereof.

16. The method of claim 10 or 11 wherein the
15 benzotriazole is polymerized onto a principal resin
selected from the group consisting of acrylate,
methacrylate, urethane, carbamate, polyester, polyether,
polystyrene, derivatized polystyrene, polyolefins, alkyd,
and epoxy polymeric resins, and mixtures thereof.

20

17. The method of claim 11 wherein the benzotriazole is
polymerized onto a principal resin comprising a hydroxy
functional acrylate resin.

25 18. The method of claim 10 or 11 further comprising a
crosslinker selected from the group consisting of
isocyanates, ureas, aminoplasts, carbamates and mixtures
thereof.

19. The method of claim 16 wherein the coating composition is crosslinked with an aminoplast crosslinking resin.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/23047

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D7/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 099 027 A (VOGL OTTO ET AL) 24 March 1992 see abstract see column 5, line 25-31 ----	1,10
A	EP 0 120 608 A (DU PONT) 3 October 1984 see abstract see page 17, line 30-33 ----	1,10
A	US 5 541 239 A (HEYWOOD JR NEWELL W) 30 July 1996 see claims; example 3 ----	1,10
A	EP 0 453 396 A (CIBA GEIGY AG) 23 October 1991 -----	1

Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search 14 April 1998	Date of mailing of the international search report 22/04/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Girard, Y

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 97/23047

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 5541239 A	30-07-96	NONE	
EP 0453396 A	23-10-91	CA 2039405 A CS 9100882 A DE 59107052 D ES 2081458 T JP 6093217 A MX 171974 B US 5106891 A	01-10-91 15-10-91 25-01-96 01-03-96 05-04-94 25-11-93 21-04-92

